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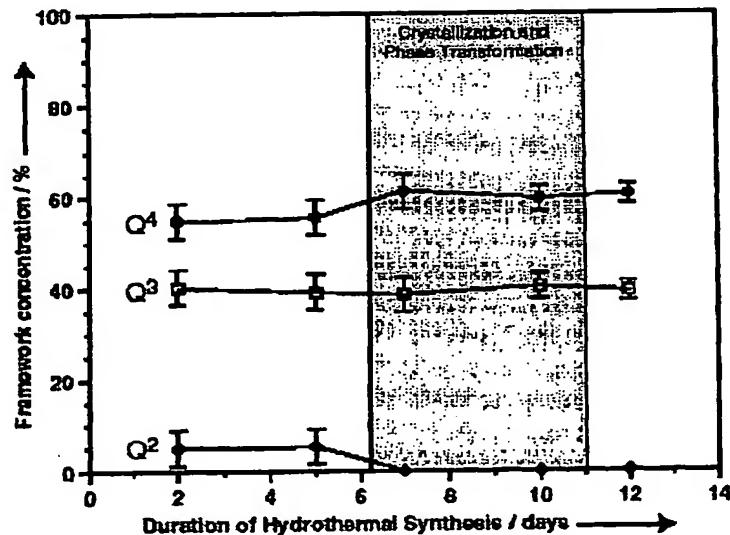
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(54) Title: SYNTHESSES OF MESOPHASE MATERIALS WITH MOLECULARLY ORDERED FRAMEWORKS



(57) Abstract: Self-assembled lamellar silica-surfactant mesophase composites have been prepared with crystal-like ordering in the silica frameworks using a variety of cationic surfactant species under hydrothermal conditions ($T>100^{\circ}\text{C}$). The crystallization of the silica is shown to result from local interactions between organic surfactants and inorganic silica. The rates of formation of the locally-ordered silica structures is shown to depend on the composition, charge density, and symmetry of charged surfactant head groups. More importantly, different charged surfactant head groups favor the formation of different local arrangements within the molecularly ordered inorganic framework and could prove valuable for tailoring the local organization of inorganic architectures of a variety of materials.

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SYNTHESSES OF MESOPHASE MATERIALS WITH MOLECULARLY ORDERED FRAMEWORKS

CROSS-REFERENCE WITH RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No.60/283,672, filed April 13, 2001.

STATEMENT REGARDING FEDERALLY FUNDED RESEARCH OR DEVELOPMENT

[0002] This invention was made with U.S. Government support under U.S. Army Research Office grant number DAAH04-96-1-0443 and the U.S. National Science Foundation grant DMR-9634396. The U.S. Government has certain rights to this invention.

FIELD OF THE INVENTION

[0003] The field of the invention is mesoscopically structured materials exhibiting molecularly ordered frameworks.

BACKGROUND OF THE INVENTION

[0004] Mesoscopically ordered inorganic materials prepared with low-molecular-weight surfactant aggregates were first discovered in 1992 by researchers at Mobil Corporation and Japan using cetyltrimethylammonium bromide ($\text{C}_{16}\text{NMe}_3^+\text{Br}^-$) as structure-directing surfactant species.[1-4] However, as discussed below, to date all such mesophase materials have been synthesized with disordered frameworks. These materials have sharply defined and adjustable pore sizes over the range 1.5 - 10.0 nm, making them attractive candidates for various applications, particularly in adsorption and catalysis. The synthesis of these materials was routinely performed under conditions that led to periodic mesostructures with amorphous inorganic frameworks that lacked long-range crystalline molecular order, as established by powder X-ray diffraction (XRD) and solid-state nuclear magnetic resonance (NMR) techniques. Many uses have been proposed for such materials, most notably in separations and catalysis and also as composite structural, electronic, and/or optical materials. However, these mesoscopically ordered materials exhibit poor mechanical and hydrothermal stabilities and poor catalytic reactivities, which are attributed to their disordered inorganic frameworks. Crystalline nanoporous materials, such as zeolites [5], by comparison, exhibit superior mechanical and thermal stabilities, compared to disordered materials, and also possess strong acid sites that are desirable for catalysis.. Previous attempts to synthesize mesophase or mesoporous materials with molecularly ordered inorganic frameworks have

proven unsuccessful. [6-9] Several efforts to use elevated temperature mesophase syntheses have resulted in the decomposition of the surfactant and subsequent formation of nanoporous zeolite materials. [10, 11] Other attempts, relying on a dual-template approach to produce mesoporous-nanoporous composites, have yielded physically separated particle mixtures of nanoporous zeolite and mesoporous material particles. [12] Pinnavaia and co-workers have used zeolite seed nanocrystals to prepare steam-stable aluminosilicate mesostructures, but these lack long range ordering. [13] Surfactant-swollen clay powders, have been prepared as polymer fillers, by taking preformed crystalline mineral powders and forming inorganic-organic powders by ion-exchange. Such clay-surfactant materials are non-templated, typically non-uniform mineral structures that are prepared with no control over framework composition or structure.¹⁴ These attempts demonstrate both the strong interest and the inherent difficulty in producing mesophase materials with molecularly ordered inorganic frameworks.

SUMMARY OF THE INVENTION

[0005] The present invention provides a method of preparing mesoscopically structured materials with molecularly ordered frameworks, which are made by combining a self-assembling agent and a network-forming precursor. For example, a self-assembled inorganic-surfactant mesophase can be prepared with crystal-like ordering of sites in the inorganic framework. This can be achieved by converting, during a hydrothermal annealing step, an initially amorphous inorganic framework of a mesoscopically structured composite into a product with a molecularly ordered inorganic framework. The method produces a crystal-like inorganic framework having long range molecular order of greater than one nanometer. Moreover, the mesoscopically structured composite formed during initial self-assembly (during the combining step) may have hexagonal, cubic, or lamellar mesostructural ordering, which separately transforms during hydrothermal treatment (the annealing step) into generally lamellar inorganic-surfactant composites that possess molecularly ordered inorganic frameworks.

[0006] Preferred self-assembly agents are amphiphilic surfactants, with a hydrophobic tail and a charged head group. Strong electrostatic interactions between structure-directing species and crystallizing precursors favor the nucleation and growth of molecular order in the resultant framework. Consequently, for negatively charged frameworks, cationic head groups, such as trialkylammonium moieties, are preferred, while for positively charged frameworks, anionic head groups are preferred. The hydrophobic tail

is preferably comprised of C₆-C₂₀ linear and branched alkyl, alkene, alkyne, phenyl, alkylphenyl, ether, or azide groups or mixtures thereof.

[0007] The inorganic network precursors can be polymerizable species, for example, silicon alkoxides, metal alkoxides, mixed metal alkoxides, organosiliconalkoxides, organometalalkoxides, hydrolyzable and condensable metal salts, and mixtures thereof. Most preferably, the inorganic species is a silica precursor, such as tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), or tetrapropoxysilane (TPOS).

[0008] For molecularly ordered silicate frameworks, the method is preferably conducted under alkaline conditions. Preferably the pH is in the range of pH 10 to pH 14.

[0009] The annealing step is preferably conducted under hydrothermal conditions for between two to forty days, depending on the choice of surfactant and solution conditions (e.g., temperature and pH). The rates of formation of the locally-ordered silicate structures depend on the composition, charge density, hydrophilicity, and symmetry of the charged surfactant head groups. For example, when the low-molecular-weight surfactant cetyltrialkylammonium bromide (CTAB) is used (with a cationic trimethylammonium head group), the annealing step for producing a molecularly ordered silicate framework takes about one to two days; for a dimethylethylammonium head group, it takes about three to seven days; for a diethylmethylammonium head group, it takes about ten to 20 days; while for a triethylammonium head group about thirteen to 25 days are required. In the mesostructured silicate-surfactant composites, two-dimensional (2D) heteronuclear correlation (HETCOR) ²⁹Si{¹H} NMR measurements show that a substantial fraction of silicon species in the molecularly ordered regions of the silicate framework regions are located within about one nanometer of the charged head groups of the structure-directing surfactant species.

[0010] Importantly, different charged surfactant head groups favor the formation of different local arrangements within the molecularly ordered inorganic framework of mesostructurally ordered solids. This is valuable for tailoring the local organization of inorganic architectures in a fashion that is analogous to that used in the syntheses of crystalline nanoporous zeolites and molecular sieves.

[0011] Mesostructurally ordered mesophases with molecularly ordered silicate networks can be produced by the present method that have amorphous silica contents that are low, i.e., below ca. 10% as estimated from the detection limits of one-dimensional (1D) ²⁹Si magic-angle-spinning (MAS) NMR. [15] Accordingly, these materials are expected to

exhibit superior mechanical and hydrothermal stabilities compared to the prior art, namely mesostructurally ordered mesophases with disordered silicate frameworks.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] **Figure 1.** A series of (a) X-ray powder diffraction patterns, (b) CP/MAS ^{29}Si NMR spectra, and (c) FTIR spectra for silica-surfactant mesophases synthesized using cetyltrimethylammonium bromide ($\text{C}_{16}\text{NMe}_2\text{EtBr}$) and annealed at 135 °C under hydrothermal conditions for different lengths of time.

[0013] **Figure 2.** 2D $^{29}\text{Si}\{\text{H}\}$ HETCOR NMR spectrum acquired for the same ordered silica- $\text{C}_{16}\text{NMe}_2\text{Et}^+$ mesophase characterized in Figure 1 (7 Days). Separate single-pulse ^{29}Si MAS and ^1H MAS spectra accompany the HETCOR contour plot along the horizontal and vertical axes, respectively. The correlations observed in the 2D HETCOR spectrum establish that all five silicon site moieties are interacting strongly with the methyl and ethyl protons of the surfactant head group. 512 acquisitions were recorded at 11.7 T for each of the 108 t_1 increments using a 3-s repetition delay.

[0014] **Figure 3.** 2D homonuclear J -coupling-correlated $^{29}\text{Si}\{^{29}\text{Si}\}$ NMR spectrum acquired for the same ordered silica- $\text{C}_{16}\text{NMe}_2\text{Et}^+$ mesophase characterized in Figure 1 (7 Days) and Figure 2. A single-pulse ^{29}Si MAS spectrum accompanies the contour plot along the horizontal axis, while the double quantum dimension lies along the vertical axis. The atomic connectivities between pairs of J -coupled ^{29}Si atoms can be established from the correlated intensities at identical double-quantum frequencies. 2048 acquisitions were recorded for each of the 96 t_1 increments using a 2-s repetition delay.

[0015] **Figure 4.** A series of CP/MAS ^{29}Si NMR spectra acquired on lamellar silica-surfactant mesophase composites synthesized using surfactants with different cationic cetyltrialkylammonium head groups under otherwise identical hydrothermal conditions at 135 °C until molecularly ordered silicate frameworks were obtained. The times required for such ordering to occur depend strongly on the charge densities of the cationic surfactant head groups, with higher charge densities promoting more rapid formation of ordered frameworks.

[0016] **Figure 5.** (a) X-ray powder diffraction patterns and (b) ^{29}Si CP/MAS NMR spectra obtained from silica- $\text{C}_{16}\text{NMe}_2\text{Et}^+$ mesophases after hydrothermal synthesis at 130 °C for 5, 7, and 12 days under otherwise identical conditions.

[0017] **Figure 6.** High-resolution transmission electron micrograph of the ordered lamellar silica- $\text{C}_{16}\text{NMe}_2\text{Et}^+$ mesophase product synthesized for 12 Days at 130 °C (see Figure 5, bottom). The corresponding, and correctly oriented, electron diffraction (ED) pattern is

shown in the upper-right-hand corner. The numbered reflections in the ED pattern correlate with corresponding planar distances observed in the TEM image, which have been enlarged.

[0018] **Figure 7.** Plots of the integrated intensities of Q^2 , Q^3 , and Q^4 ^{29}Si framework species in the silica- $\text{C}_{16}\text{NMe}_2\text{Et}^+$ mesophases as functions of the duration of hydrothermal synthesis. The shaded area represents the period when the initially hexagonal mesophase with its amorphous silicate framework transforms into a lamellar mesophase with a locally ordered silicate framework.

[0019] **Figure 8.** Comparison of materials made according Inagaki et al [16] versus the materials shown in Figure 1 (7 days). The XRD of Inagaki et al. (A) shows no apparent diffraction from the silica framework as well as narrow and intense XRD peaks at high scattering angles. In contrast (B), derived from Figure 1, shows diffraction from the silicate framework and narrow but weak XRD reflections at high scattering angles. Moreover, the ^{29}Si NMR data of Inagaki, et al. (C) exhibits broad ^{29}Si NMR peaks ($\Delta \sim 10$ ppm), whereas corresponding data from Figure 1 (D) exhibits narrow ^{29}Si NMR peaks ($\Delta \sim 1$ ppm) indicating a high degree of molecular ordering throughout the sample.

DETAILED DESCRIPTION

I. General Purpose or Utility

[0020] Inorganic-organic mesophases with crystalline inorganic frameworks hold great promise for applications as coatings, films and barriers, in catalysis, adsorption and separation, as optical host materials, in electronic devices, and as structural materials. However, until now, inorganic-organic mesophases and mesoporous solids have been synthesized with frameworks that lack long range (> 1 nm) molecular order. [4, 6-8] The often harsh conditions to which many coatings, films, catalysts, separation agents, optical, electronic, and structural materials are exposed require robust materials that do not degrade under mechanical wear or hydrothermal conditions. Mesophase composites with molecularly ordered frameworks possess enhanced mechanical and hydrothermal stabilities and are expected to lead to materials with superior structural, reaction, and/or optoelectronic properties. The insights on which these materials are based are expected to lead to superior coatings, films, barriers, catalysts and separation agents, particularly, but not exclusively, for large molecules, additives for structural materials, such as reinforced polymers, personal care products, electronic and optical materials.

II. Technical Description

[0021] The present application is directed to an improved preparation of self-assembled inorganic/organic composites, in which an inorganic framework assumes crystal-like molecular ordering. These materials are prepared by combining a self-assembling organic species, such as an amphiphilic surfactant (preferably, but not necessarily a cationic surfactant) with a network-forming inorganic precursor species, (preferably, but not necessarily silica precursors). Self-assembly refers to a process in which molecular moieties segregate according to thermodynamic partitioning criteria (e.g., lyotropic liquid crystals or as defined by the Flory-Huggins χ parameter for block copolymers) or the packing of macroscopic components (e.g., the organization of densely assembled latex spheres). For the case at hand, the surfactant species act as structure-directing agents for the inorganic precursor species, which polymerize initially into a typically amorphous inorganic network with initially hexagonal, cubic, or lamellar mesoscopic order cooperatively imparted by interactions among the self-assembled surfactant and inorganic species. Mesoscopic order in a material is established by an X-ray diffraction (XRD) pattern with at least one reflections that corresponds to a d spacing of >2 nm. (See also IUPAC). Upon annealing under hydrothermal conditions, the composite transforms into a lamellar mesophase with a molecularly ordered inorganic framework structure. High degrees of molecular order in the inorganic framework are established by narrow peaks (<2 ppm) in solid-state magic-angle spinning ^{29}Si NMR spectra of siliceous silicate/surfactant materials [16] and high-angle (>20°) reflections in X-ray or electron diffraction patterns (see accompanying Figures).

[0022] An inorganic network precursor-surfactant composite can typically be prepared at room temperature using the following molar compositions: 1.0 M inorganic precursor, 0.01 - 10.0 M surfactant, and sufficient base compound to give an alkaline pH. A typical synthesis procedure involves dissolving an appropriate amount of surfactant in water, after which the base compound, and optionally a water-miscible organic solvent, is added. After stirring the solution for about 30 min, the inorganic precursor is then added and the solution stirred for another 30 min, after which time the pH may be lowered to about 11 to 11.5 with concentrated acid. After about 2 h of stirring, each mixture is transferred into reaction vessels, sealed, and placed in an oven at about 130-135 °C.

[0023] The inorganic framework precursors can include silicon alkoxides, metal alkoxides, mixed-metal alkoxides, organosiliconalkoxides, metal salts, organometalalkoxides and mixtures thereof. Preferred inorganic precursor species, include tetraethoxysilane

(TEOS), tetramethoxysilane (TMOS), tetrapropoxysilane (TPOS), or organically modified derivatives, which are suitable sources of silica for the preparation of silica structures. In addition, the metal-containing precursors may include any of the main group, transition metals, rare-earth metals and mixtures thereof. "Transition metal", as used herein, refers to an element designated in the Periodic Table as belonging to Group IIIIB (e.g., scandium and yttrium), Group IVB (e.g., titanium, zirconium and hafnium), Group VB (e.g., chromium, molybdenum and tungsten), Group VIIIB (e.g., manganese, technetium and rhenium), Group VIIIIB (e.g., iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium and platinum), Group IB (e.g., copper, gold and silver) and Group IIB (zinc, cadmium and mercury). In addition, the precursors of inorganic frameworks, such as Nb₂O₅, TiO₂, ZrO₂, WO₃, AlSiO_{3.5}, AlSiO_{5.5}, SiTiO₄, Al₂O₃, Ta₂O₅, SiO₂, SnO₂, HfO₂, ZrTiO₄, and Al₂TiO₅, rare earth oxides, metal oxynitrides, metal oxychalcogenides, metal nitrides, or metal chalcogenides are considered to be within the scope of the present invention.

[0024] The formation of highly ordered frameworks is strongly influenced by the choice of surfactants. In particular, the head groups of the surfactant species will determine the particular structure obtained. A preferred surfactant is comprised of a charged head group and a hydrophobic tail. Most preferably, the charged head group will be a cationic head group, such as trialkyammonium, trispyrrolidinium. The hydrophobic tail is preferably C₈-C₂₀ linear and/or branched alkyl, alkene, alkyne, phenyl, alkylphenyl, ether, or azide groups, and mixtures thereof. A most preferred surfactant is a cetyltrialkylammonium bromide. Alternatively, the surfactant can be an amphiphilic block copolymer, anionic and nonionic detergents, and mixtures of the foregoing.

[0025] A base compound is typically included in an amount sufficient to give an alkaline pH and/or to adjust the ionic strength of the mixture. Preferred base compounds include alkylammonium hydroxides, ammonium hydroxide, and alkali metal hydroxides, such as NaOH, KOH, etc. Moreover, an acid, such as HBr, may be utilized to lower the pH to within a preferred range. Preferably, the pH of the mixture will be about pH 10-14. Most preferably, the pH range is about pH 11-11.5. Optionally, the mixture may also include one or more organic solvents, preferably a water-miscible alcohol, such as methanol or ethanol, or a partially water-miscible or water-immiscible organic solvent, such as benzene, trimethylbenzene, hexanol, or hexane, as a hydrophobic swelling agent.

[0026] The annealing step is conducted by hydrothermal treatment at about 100 to 140 degrees Celsius, preferably about 130-135 degrees Celsius. The length of the hydrothermal treatment required to form a highly ordered inorganic framework will depend

on the choice of surfactants. For example, when annealing a silica/cetyltrialkylammonium bromide composite, the length of the annealing step will depend on the combination of alkyl groups present in the head group of the surfactant as follows: trimethyl<dimethylethyl<diethylmethyl<triethyl <tripropyl. The annealing temperature should be below the temperature at which significant thermal decomposition of the structure-directing surfactant species occurs. For more thermally stable surfactants, higher annealing temperatures would be possible.

III. Example I

[0027] Self-assembled silicate-surfactant mesophase composites were prepared with molecularly ordered inorganic frameworks under alkaline, hydrothermal conditions. The formation of such highly ordered frameworks was strongly influenced by the head groups of the surfactant species, which determined the particular structure obtained. Various surfactant species have been used to illustrate this point, leading to a variety of molecularly ordered inorganic framework structures. Specifically, the charge density, charge distribution, and hydrophilicity of the surfactant head group species, for example, cationic trialkylammonium moieties, were systematically varied by modifying the type and combination of the alkyl moieties present using methyl, ethyl, and propyl groups.

A. Methods

1. Surfactant Syntheses.

[0028] The cationic surfactants, cetyltrimethylammonium bromide ($C_{16}NMe_3Br$) and cetyltrimethylethylammonium bromide ($C_{16}NMe_2EtBr$), were purchased and required no further preparation. Other closely related surfactants, $C_{16}NMeEt_2Br$, $C_{16}NEt_3Br$, and $C_{16}NPr_3Br$, were synthesized from cetyl bromide, $C_{16}Br$, and an excess of the appropriate alkylamine (*i.e.*, $NMeEt_2$, NEt_3 , and NPr_3 , where $Me = -CH_3$, $Et = -C_2H_5$, and $Pr = -C_3H_7$.) The reactants were refluxed for 3-5 days in an ethanolic solution and recrystallized from ethanol/ethyl acetate (3x). [12]

2. Lamellar Mesophase Syntheses.

[0029] Tetramethylammonium hydroxide (TMAOH, 25 wt% in H_2O), hydrobromic acid (HBr), methanol (CH_3OH), and tetramethylorthosilicate (TMOS) were used as received from Aldrich. Lamellar silica-surfactant composites were prepared at room temperature using the following molar compositions: 1.0 SiO_2 : 0.7 surfactant : 0.7 TMAOH : 113.4 H_2O : 9.9 CH_3OH . A typical synthesis procedure involved dissolving an appropriate amount of surfactant in water, after which TMAOH and CH_3OH were added and the solution

stirred for 30 min. TMOS was then added and the solution stirred for another 30 min, after which time the pH was lowered to 11.5 with concentrated HBr. After 2 h of stirring, each mixture was aliquoted into a number of identical Teflon-lined Parr reaction vessels, sealed, and placed in an oven at 135 °C. The reaction vessels were individually removed from the oven after specified intervals of time and then allowed to cool to room temperature. The mesophase precipitates were subsequently washed with deionized water to remove any excess surfactant and/or solvents.

B. Results

[0030] Figure 1 presents structural characterization data of silica-C₁₆NMe₂Et⁺ composites monitored as a function of time to follow the process of framework ordering. The X-ray diffraction (XRD) pattern and broad ²⁹Si MAS NMR peaks in Figures 1(a,b) show that the sample is initially a lamellar mesophase with a locally disordered silica framework. Longer hydrothermal treatment of this composite leads to improved resolution in the ²⁹Si MAS spectrum (Figure 1(b), 7 Days), with the ²⁹Si peak linewidths narrowing to 1 ppm or less. The appearance of the five well-resolved ²⁹Si NMR peaks is accompanied by the presence of both low- and high-angle reflections in the powder X-ray diffraction pattern. This is indicative of molecular ordering in the silicate sheets and likely accompanying organization of the surfactant head groups between the inorganic layers.

[0031] The novel framework structure has been characterized and shown to be a single phase material. The different ²⁹Si sites are interconnected via bridging oxygen atoms and are molecularly proximate to the structure-directing surfactant species. This is unambiguously established by using solid-state 2D NMR methods. For example, 2D ²⁹Si{¹H} heteronuclear correlation (HETCOR) NMR measurements provide detailed insight on interfacial molecular interactions between different ²⁹Si sites and the proton-containing amphiphilic surfactant species. The results shown in Figure 2 provide unambiguous evidence that a substantial fraction (if not all) of the five different ²⁹Si species are molecularly adjacent (< 1 nm) to the cationic head groups of the structure-directing C₁₆NMe₂Et⁺ surfactant species, consistent with incorporation of the different ²⁹Si sites into the molecularly ordered inorganic framework of the material. For materials with high degrees of molecular order, molecular site connectivities can be established using the 2D solid-state INADEQUATE NMR technique. The ²⁹Si INADEQUATE NMR experiment relies upon homonuclear J-couplings between covalently bound ²⁹Si nuclei to establish the adjacency of different sites in the siliceous framework structure. For example, from the intensity correlations in the ²⁹Si INADEQUATE NMR spectrum in Figure 3, the ordered framework of the silica-C₁₆NMe₂Et⁺

composite is shown to be a highly interconnected silicate network, with intimately mixed Q^3 and Q^4 species that are not separated into distinct domains. These results confirm that the highly ordered silica framework of the silica- $C_{16}NMe_2Et^+$ composite is comprised of a densely interconnected network.

[0032] To examine generally the role(s) of cationic surfactant head groups in inducing molecular order in silica frameworks, cetyltrialkylammonium bromide surfactants with different alkylammonium moieties were used to prepare layered silicate-surfactant mesophases under otherwise identical alkaline conditions. Subtle modifications to the head groups of surfactant species (e.g., replacing one of the three methyl groups with an ethyl moiety) alters the local charge density and changes its distribution. The ^{29}Si MAS NMR spectra of lamellar silica-surfactant composites obtained after extended hydrothermal treatments with different cationic trialkylammonium head groups are shown in Figure 4. Figures 4a and 4b show the ^{29}Si MAS spectra of mesoscopically ordered materials with different molecularly ordered inorganic frameworks obtained using $C_{16}NMe_3^+$ and $C_{16}NMe_2Et^+$, respectively. When the trialkylammonium head group of the cationic surfactant was modified to include a single methyl and two ethyl group moieties, $C_{16}NMeEt_2^+$, a lamellar composite with an amorphous silica framework again resulted after hydrothermal syntheses lasting as long as 9 days, as evidenced by XRD and ^{29}Si MAS NMR results (not shown here). As with the two previous cases, the silica- $C_{16}NMeEt_2^+$ composite similarly transformed into a product with a highly ordered silicate framework. This process began after approximately 10 days under hydrothermal conditions and was completed after 19 days, as evidenced by the ^{29}Si MAS spectrum in Figure 4c, which contains no discernible signal from amorphous silica. The lengthened hydrothermal treatment is consistent with the lower charge density of this cationic surfactant head group, which is expected to interact more weakly with the anionic silicate framework. When three ethyl or three *n*-propyl groups are present producing even larger cationic trialkylammonium surfactant head groups, still weaker, though symmetric, charge density distributions result. Consistent with the results presented above, silicate-surfactant composites take substantially longer to form molecularly ordered inorganic frameworks, as the size of the cationic trialkylammonium head groups increases and the charge density is reduced.

IV. Example II

[0033] In this example, 2D crystallization of the inorganic framework is shown to promote mesoscopic phase transitions, in this case, from an initial hexagonal mesostructure to

a lamellar architecture. Specifically, two-dimensional (2D) crystallization of an initially amorphous silica framework in a hexagonal mesophase composite induces a transition to a stable lamellar material with a molecularly ordered silicate lattice.

A. Methods

[0034] The silica-surfactant mesophase samples were all prepared using a molar composition and conditions that favor the initial formation of hexagonally ordered mesophase composites: 1.0 C₁₆NMe₂EtBr : 0.5 NaOH : 1.0 TEOS : 150 H₂O. They were synthesized by combining appropriate amounts of C₁₆NMe₂EtBr, H₂O, and NaOH and stirring until the surfactant dissolved, after which TEOS was added and the solution stirred for 30 min. The pH of the solution was then adjusted to 11.0 using 2M NaOH and the solution stirred for an additional 30 min. The mixture was transferred into separate stainless steel autoclaves (Parr) and placed in a temperature controlled oven at 130 °C. These reaction vessels were individually removed from the oven after specified intervals of time and then allowed to cool to room temperature. The mesophase precipitates were subsequently washed with deionized water to remove excess surfactant and/or solvents.

[0035] X-ray powder diffraction (XRD) data were acquired on a Scintag PAD X diffractometer using Cu-K_α radiation and a liquid-nitrogen-cooled germanium solid-state detector. The data were collected from 1° to 35° (2θ), with a resolution of 0.02° and a count time of 5 s at each point.

[0036] Solid-state ²⁹Si NMR experiments were performed at ambient temperature under conditions of magic-angle-spinning (MAS). The cross-polarization (CP) experiments were acquired on a Chemagnetics CMX-180 spectrometer (4.2 T) using a pulse-delay of 3 s and spinning at 5 kHz. Single-pulse ²⁹Si MAS NMR experiments were acquired on a Chemagnetics CMX-500 spectrometer (11.7 T) using a 500 s pulse-delay while spinning at 7 kHz. Continuous wave ¹H decoupling was applied during the acquisition of all spectra. ²⁹Si chemical shifts are referenced to tetramethylsilane (TMS).

[0037] For the transmission electron microscopy measurements, the sample was ultrasonically dispersed in ethanol (99.9 vol%) and the dispersion subsequently deposited onto a carbon microgrid. High-resolution electron microscopy (HREM) images were acquired using a 400 kV electron microscope (JEM-4000EX) at room temperature.

B. Results

[0038] Using solid-state ²⁹Si NMR spectroscopy and powder X-ray diffraction, the molecular and mesoscopic changes occurring during this transformation can be

established and correlated. For example, Figure 5 displays the results for a series of silica-surfactant (cetyltrimethylammonium, $C_{16}NMe_2Et^+$) mesophases prepared under identical hydrothermal conditions at 130 °C for various lengths of time. Initially, a hexagonally ordered material (MCM-41) is obtained, as evidenced by XRD reflections at 4.46 (100), 2.59 (110), 2.24 (200) and 1.69 nm (210) shown in Figure 5(a), 5 Days. The silica framework, although mesoscopically ordered, however, is locally amorphous, as evidenced by the broad ^{29}Si NMR linewidths (Figure 5(b), 5 Days) and the absence of high-angle XRD reflections. The broad ^{29}Si linewidths reflect locally heterogeneous environments arising from a distribution of bond lengths and/or bond angles that are common to locally amorphous silica networks. [15]

[0039] No significant changes in reaction solution pH, dissolved silicate concentration, or silicate speciation were observed during the mesophase transformation and framework ordering processes. Within the sensitivity limits of the measurements, the pH of the reaction solution was observed to be constant ($pH 11.0 \pm 0.1$). Similarly, solution-state ^{29}Si NMR spectra showed no significant changes in signal-to-noise (concentration) or in the resonant signals present (speciation) during the course of the synthesis. Predominant ^{29}Si signals were observed at -71.6 ppm from dilute monomeric species and much weaker signals from dimer species in the vicinity of -80 ppm.

[0040] As the duration of the hydrothermal silica- $C_{16}NMe_2Et^+$ synthesis is increased to seven days, the hexagonal mesophase begins to transform into a lamellar phase with a substantially higher degree of molecular ordering in the silica framework. This phase transformation is evident in the powder XRD pattern (Figure 5(a), 7 Days), which shows $hk0$ reflections at 4.64 (100), 2.70 (110), 2.34 (200), and 1.78 nm (210) that are characteristic of hexagonally ordered MCM-41, along with $h00$ reflections at 3.76 nm (100) and 1.85 nm (200) corresponding to the appearance of a lamellar mesophase. The ^{29}Si CP/MAS NMR spectrum for this sample (Figure 5(b), 7 Days), furthermore, displays five resolvable peaks at -96.9, -100.7, -103.5, -108.9, and -114.4 ppm, as well as a broad distribution of resonances over the range -90 to -115 ppm. These five distinct ^{29}Si resonances are identical to those previously observed in the locally-ordered lamellar mesophase materials of Example 1, which have been assigned to distinct Q^3 (-96.9 and -100.7 ppm) and Q^4 (-103.5, -108.9, and -114.4 ppm) ^{29}Si framework species. Using Gaussian line-fitting techniques on a single-pulse ^{29}Si NMR spectrum, the relative fraction of molecularly ordered silica is approximately 15% of the total silica present, consistent with estimates from the XRD measurements. The ^{29}Si NMR

results thus indicate the presence of both amorphous and molecularly-ordered ^{29}Si species, which appear to be associated separately with the hexagonal and emerging lamellar phase, respectively.

[0041] Extending the duration of hydrothermal synthesis beyond seven days further promotes the hexagonal-to-lamellar phase transformation and accompanying molecular ordering of the silica-C₁₆NMe₂Et⁺ framework. After 12 days, the powder XRD pattern for this sample (Figure 5(a), 12 Days) displays three *h00* reflections at 3.11, 1.57 and 1.06 nm, typical of a lamellar mesophase, with no evidence of a co-existing hexagonal component. Several high-angle XRD reflections are also visible, characteristic of a molecularly-ordered inorganic lattice. [17] The ^{29}Si CP/MAS NMR spectrum for this sample contains the same five distinct and narrow (0.8-1.2 ppm FWHM) resonances previously observed after 7 days of hydrothermal treatment, reflecting crystal-like molecular ordering of the 2D silicate sheet framework. There is no evidence of an amorphous silica fraction nor hexagonal mesophase remaining.

[0042] High resolution transmission electron microscopy (TEM) provides corroborative evidence for correlated mesophase and framework structural reorganization. Figure 6 shows a TEM image and the corresponding electron diffraction (ED) pattern of the final lamellar silica-C₁₆NMe₂Et⁺ product (Figure 5, 12 days), revealing for the first time imaging evidence of molecularly ordered framework atoms in synthetic inorganic-organic mesophase composites. Three different planar distances are clearly observed in the TEM image and the ED pattern, manifested by the three characteristic lengths and spotty arcs labeled "1", "2", and "3" in Figure 6. The planar distances calculated from the ED pattern and the TEM image at locations "1", "2", and "3" are 2.6, 1.3, and 0.9 nm, respectively. The scattering intensities at 2.6 and 1.3 nm are likely the *100* and *200* reflections resulting from the lamellar organization of the material. These distances are somewhat smaller than the corresponding distances derived from powder XRD (Figure 5(a), 12 Days), which may be attributable to reduced interlayer spacing due to partial decomposition of the organic species in the intense electron beam or from the partial extraction of surfactant molecules during the preparation of the TEM sample with ethanol. The scattering intensity at 0.9 nm ("3") cannot be assigned to the *300* reflection, because in the 2D ED pattern it appears in a different diffraction plane than that common to the "1" and "2" reflections. In addition, the reflection at 0.9 nm is substantially sharper and agrees well with the narrow powder XRD reflection at 0.85 nm (Figure 5(a), 12 Days) that is attributed to intra-framework order. The TEM,

electron diffraction, and XRD results thus corroborate ordering over mesoscopic and molecular length scales in the lamellar silica-C₁₆NMe₂Et⁺ composites.

[0043] To assess the different relative roles of framework crystallization and changes in the extent of silica condensation on the hexagonal-to-lamellar phase transformation, single-pulse solid-state ²⁹Si magic-angle-spinning (MAS) NMR spectra (not shown here) were acquired and used to provide quantitative estimates of the different ²⁹Si species present. The ²⁹Si resonances from each MAS spectrum were integrated using standard Gaussian line-fitting techniques [18, 19], and the normalized concentrations of the Q², Q³, and Q⁴ silicate species are shown in Figure 7 as functions of synthesis time. The plots associated with the Q³ and Q⁴ moieties, establish that their relative concentrations do not vary substantially before, during, or after the phase change and crystallization of the 2D silicate sheets. A slight increase (ca. 5%) in the concentration of Q⁴ species is observed at the onset of the phase transformation, in conjunction with a simultaneous and equivalent decrease in Q² silica species. This is consistent with minor densification of the samples expected during 2D crystallization of the silicate framework. [20-22] Such a small variation in the extent of framework condensation is not likely alone to account for the mesophase transition observed.

[0044] Rather the hexagonal-to-lamellar mesophase transformation appears to be caused predominantly by the formation of molecularly ordered silicate sheets in the composite framework. Analyses of the underlying thermodynamics and associated relative energies of the different mesophases, amorphous silica, and crystalline siliceous zeolites support this. In particular, the enthalpy differences between an amorphous silica glass and crystalline open-framework zeolites are ca. 17-170 J/g (~1-10 kJ/mol). [22,23] This significantly exceeds the enthalpy changes accompanying mesophase transformations of self-assembled organic systems, which are on the order of 1 J/g. [24, 25] While enthalpy and entropy differences exist between self-assembled hexagonal and lamellar surfactant mesophases (due to electrostatic, van der Waals, steric interactions, etc.), they are on balance smaller than the enthalpy and entropy changes of the silicate framework as it progresses to an ordered structure. The framework ordering and mesophase transformation processes are spontaneous, though occur slowly (ca. weeks). Such time scales are similar to those observed for the crystallization of zeolites and are much slower than typically associated with mesophase transitions involving low-molecular weight surfactants. These observations are consistent with thermodynamic studies of zeolite crystallization [23], reflecting the slow, but

spontaneous, ordering of high-surface-area silicate lattices in the presence of structure-directing molecular species.

[0045] These results establish that 2D crystallization of initially locally disordered silica-surfactant frameworks can induce transitions from hexagonal to lamellar mesophase structures. This is the first time that such phase transitions have been observed to derive from framework ordering processes, as opposed to changes in the hydrophobic volumes of surfactant aggregates or polymerization of inorganic species. [26] In this case, the favorable energetics associated with ordering of the silica framework in the presence of cationic surfactant species cause the inorganic component to adopt the primary mesostructure-directing function, rather than the surfactant species. Indeed, similar results have also been found for mesophase transitions from cubic mesostructures with amorphous silica walls to lamellar composites with molecularly ordered silicate frameworks, pointing to the generality of this phenomenon (data not shown). The resulting composite solids thus adopt layered framework structures that are similar to, but distinct from, numerous naturally occurring phyllosilicate minerals [27,28], according to differences in the surfactant head group moieties. Such framework ordering provides increased mechanical and thermal stability to inorganic-organic composite materials. In addition, understanding the associated self-assembly and crystallization mechanisms allows not only mesoscopic organization, but also molecular order, of mesostructured materials to be controlled with important implications for the synthesis of new catalysts and adsorbents.

V. Description of the Best Way to Practice the Invention

[0046] The molecular organization of the inorganic silica in these materials is dependent upon the organic template species used, the pH/ionic strength of the synthesis mixture, as well as the temperature and pressure employed. A key aspect is the strength of the interactions, particularly electrostatic, between the inorganic framework and surfactant head group species, which can be controlled by adjusting the pH or ionic strength of the synthesis solution, along with mixture composition. Strong interactions promote the formation of ordered inorganic frameworks. For a given pH, the charge-density of the head groups exert a strong influence on the rate at which molecular framework order develops: higher head group charge-densities result in more rapid formation of molecularly ordered inorganic networks. Furthermore, different molecularly ordered framework structures are produced according to the different interactions presented by different structure-directing head group moieties. Synthesis temperature also plays a crucial role in the formation of these

ordered networks. For example, elevated temperatures facilitate the rate at which the ordered networks form, although excessively high temperatures (>140 °C) can lead to the decomposition of the surfactant, causing a subsequent degradation of framework order. In these cases, the remnants of the structure-directing surfactant species exert a weak influence on the inorganic architecture, resulting in materials that are mesoscopically and locally disordered. These results emphasize the importance of the hydrothermal synthesis temperature, the pH/ionic strength, and the charge density and hydrophilicity of the surfactant head group species on the structure of the molecularly ordered inorganic framework.

VI. Possible Modifications and Variations of the Best Way

[0047] The previously mentioned results use silica as the polymerizable inorganic species and various cetyltrialkylammonium bromide molecules as the structure-directing surfactant species. A wide variety of inorganic species have been incorporated into the disordered inorganic frameworks of mesophase materials and are expected to be able to be incorporated into molecularly ordered inorganic frameworks of mesophase materials, according to the art taught here. This includes especially inorganic framework species that appear in synthetic zeolites and molecular sieves, including aluminosilicates, titanosilicates, borosilicates, gallosilicates, aluminophosphates, borophosphates, metallo-phosphates, metallo-borophosphates, siliconaluminophosphates, metallo-germanates. In addition, semiconductor compounds synthesized as surfactant-organized nanocrystals should be preparable as continuous 2D and/or 3D mesophases with molecularly ordered frameworks. Similarly, this art is expected to apply to wholly organic mesophase systems [29], in which strongly interacting self-assembling species interact with and may direct the nucleation and growth of molecularly ordered *organic* frameworks from charged organic precursor species.

[0048] In addition, this invention applies to self-assembling agents generally, provided sufficiently strong interactions exist between the framework and self-assembling agent across their common interface. Although only a few surfactants were used in the studies presented here, their influence on the molecular ordering of the final inorganic material can be extended to a variety of other self-assembling agents, including oligomeric surfactants (cationic, anionic, non-ionic), block-copolymers, emulsions, or monodispersed macroscopic (> 500 nm) objects, such as polymer or silica spheres, rods, disks, or other shapes. Mesoporous materials have been synthesized with block copolymers, many varieties of surfactants, and even biological macromolecules, which could be used to produce mesophase composites with molecularly ordered inorganic frameworks. The key

requirement is that the inorganic and organic species must interact with sufficient strength that molecular ordering is promoted in the inorganic framework along with mesoscopic ordering. Different structure-directing moieties (*e.g.*, all those used for synthesizing crystalline zeolites and molecular sieves) can be incorporated into the self-assembly agents to induce molecular organization of a mesophase framework. In addition to the cationic species discussed above, anionic moieties (*e.g.*, phosphates, sulfates), non-ionic moieties (*e.g.*, amines), amino acids, 1,4-diazabicyclo[2.2.2]octane (DABCO) derivatives, and mixtures thereof, can be used, with solution conditions (temperature, pH, ionic strength) adjusted accordingly to promote the strong framework-organic interactions required. These species can be incorporated as oligomers, as pendant groups on copolymer blocks or on the surfaces of macroscopic objects, such as surface-functionalized polystyrene or silica spheres. Such template-functionalized meso- or macroscale self-assembly agents would allow molecularly ordered nanoporosity to be combined with meso- or macroporosity in these materials. The techniques described herein may thus aid in inducing local crystallization within the framework of meso- or macroporous materials, while preserving porosity. Such procedures could also be applied on a variety of other porous substrates with the goal of inducing local order.

[0049] The work described herein produced mesophase composites from oligomeric silica solutions, however, other functionalized monomeric or oligomeric metal oxide species or other inorganic or organic species could be used. Inorganic materials exhibiting meso- and/or macroscopic organization without local framework order could also be amenable to post-synthesis treatment, according to the criteria described, to induce framework ordering. Post-synthesis grafting, functionalization, and pillaring of the materials are possible. This includes two-step processing. For example, a first step could take place under acidic conditions to spin-coat inorganic-surfactant films, followed by subsequent hydrothermal treatment under adjusted alkaline conditions to anneal molecular framework order in transparent films. Such materials are anticipated to have enhanced mechanical strength and thermal stability for uses as barrier materials (for controlling permeability in membranes or protective coatings for organic light-emitting diodes) and optical host matrices for optically responsive guest species. In summary, mesophase materials can be prepared with structure-directing surfactants or agents that yield local and/or long range crystal-like ordering in their frameworks by using suitable annealing treatment.

VII. Advantages and improvements over existing practices & features believed to be new

[0050] Currently, the only methods, other than those presented here, used to produce locally-ordered inorganic-organic composites with regular ($> 1 \text{ nm}$) order yield nanostructured zeolites or molecular sieves without mesoscopic organization [5, 30] or surfactant-swollen clay powders, which are non-templated non-uniform mineral structures without control of material composition or structure. [14, 30] Mesostructured materials have been prepared with templated zeolite nanocrystal seeds, yielding walls that may or may not contain small ($< 1 \text{ nm}$) nanocrystallites, though without longer range molecular order. Very recently, Inagaki *et al.*, have prepared mesoporous organosilica materials with apparently ordered organic phenyl groups in the walls, though the silicon sites in the inorganic framework are not ordered [16]. (See Figure 8). These methods have failed to produce mesophase materials with high degrees of molecular ordering in the frameworks due to the absence of strong templating interactions with the structure-directing species or ineffective hydrothermal annealing treatments used in those preparations. All chemical syntheses of mesoporous or inorganic-organic composite mesophase materials have thus far produced mesoscopically ordered materials with disordered inorganic frameworks.

[0051] The references listed in the following Bibliography are all incorporated herein by reference.

BIBLIOGRAPHY

- [1] Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* 1992, 359, 710-712.
- [2] Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, T. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* 1992, 114, 10834-10843.
- [3] Degnan, T. F.; Johnson, I. D.; Keville, K. M. *US Patent No. 5,156,828*, 1992
- [4] Inagaki, S., Fukushima, Y., Kuroda, K. *J. Chem. Soc., Chem. Commun.*, 1993, 680.
- [5] Davis, M.E., Lobo, R.F. "Zeolite and Molecular Sieve Synthesis," *Chem. Mater.*, 1992, 4(4), 756-768.

- [6] Sayari, A. *Chem. Mater.* **1996**, *8*, 1840-1852.
- [7] Zhao, H.; Nagy, K. L.; Waples, J. S.; Vance, G. F. *Environ. Sci. Technol.* **2000**, *34*, 4822-4827.
- [8] Wu, J.; Groass, A. F.; Tolbert, S. H. *J. Phys. Chem. B.* **1999**, *103*, 2374-2384.
- [9] Huo, Q.; Zhao, D. Y.; Feng, J. L.; Weston, K.; Burrato, S. K.; Stucky, G. D.; Schacht, S.; Schueth, F. *Adv. Mater.* **1997**, *9*, 974.
- [10] Beck, J. S.; Vartuli, J. C.; Kennedy, G. J.; Kresge, C. T.; Roth, W. J.; Schramm, S. E. *Chem. Mater.* **1994**, *6*, 1816-1821.
- [11] Chen, X.; Huang, L.; Quanzhi, L. *J. Phys. Chem.* **1997**, *101*, 8460-8467.
- [12] Huang, L.; Guo, W.; Deng, P.; Xue, Z.; Li, Q. *J. Phys. Chem.* **2000**, *104*, 2817-2823.
- [13] Liu, Y., Zhang, W.Z., Pinnavaia, T.J. *J. Am. Chem. Soc.*, **2000**, *122*(36) 8791-8792.
- [14] *Polymer-clay nanocomposites*, Pinnavaia, T.J. and Beall, G.W., eds., Wiley: New York, 2000.
- [15] Engelhardt, G., Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; John Wiley & Sons: New York, 1987.
- [16] Inagaki,S., Guan, S., Ohsuna, T., Terasaki, O. *Nature*, **2002**, *416*, 304.
- [17] S. C. Christiansen, D. Zhao, M. T. Janicke, C. C. Landry, G. D. Stucky, B. F. Chmelka, *J. Am. Chem. Soc.* **123** (2001) 4519.
- [18] G. E. Maciel, D. W. Sindorf, *J. Am. Chem. Soc.* **102** (1980) 7607.
- [19] S. Leonardelli, L. Facchini, C. Fretigny, P. Tougne, P. A. Lagrande, *J. Am. Chem. Soc.* **114** (1992) 6412.
- [20] J. Xu, Z. Luan, H. He, W. Zhou, L. Kevan, *Chem. Mater.* **10** (1998) 3690.
- [21] C. A. Fyfe, G. Fu, *J. Am. Chem. Soc.* **117** (1995) 9709.

- [22] A. Navrotsky, *Rev. Mineral.* 32 (1995) 121.
- [23] I. Petrovic, A. Navrotsky, M. E. Davis, S. I. Zones, *Chem. Mater.* 5 (1993) 1805.
- [24] B. Stühn, *J. Polym. Sci. B, Polym. Phys.* 30 (1992) 1013.
- [25] H. Kasten, B. Stühn, *Macromol.* 28 (1995) 4777.
- [26] A. F. Gross, E. J. Ruiz, S. H. Tolbert, *J. Phys. Chem. B.* 104 (2000) 5448.
- [27] J. M. Garces, S. C. Rocke, C. E. Crowder, D. L. Hasha, *Clays and Clay Minerals* 36 (1988) 409.
- [28] G. G. Almond, R. K. Harris, K. R. Franklin, *J. Mater. Chem.* 7 (1997) 681.
- [29] Hillmyer, M.A., Lipic, P.M., Hajduk, D.A., Almdal, K., Bates, F.S. *J. Am. Chem. Soc.*, 1997, 119, 2749.
- [30] Ma, Y., Tong, W, Zhou, H., Suib, S.L, " Review of Zeolite-Like Porous Materials" *Microporous and Mesoporous Materials*, 2000, 37, 243-252.

What is claimed is:

1. A method of forming a mesoscopically structured material with a molecularly ordered framework, comprising:
 - i) combining a self-assembly agent and network-forming precursor species under conditions effective to form a mesoscopically structured material; and
 - ii) treating said mesoscopically structured material to form a mesoscopically structured product containing a molecularly ordered framework.
2. The method of claim 1, wherein said molecularly ordered framework is an inorganic network.
3. The method of claim 2, said molecularly ordered inorganic network being ordered for a length of greater than one nanometer.
4. The method of claim 2, wherein said molecularly ordered framework is a crystalline inorganic network.
5. The method of claim 2, said mesoscopically structured material formed during the combining step having an amorphous inorganic framework.
6. The method of claim 1, wherein said self-assembly agent is selected from the group consisting of amphiphilic surfactants, block-copolymers, emulsions, monodispersed polymer and silica spheres.
7. The method of claim 6, wherein said self-assembly agent is amphiphilic.
8. The method of claim 7, wherein said self-assembly agent is a surfactant comprising a hydrophobic tail and a charged head group.
9. The method of claim 8, wherein said charged head group is cationic.
10. The method of claim 9, wherein said cationic head group is a trialkylammonium moiety.
11. The method of claim 8, wherein said hydrophobic tail is selected from the group consisting of linear or branched C₁-C₂₀ alkyl, alkenyl, alkynyl, phenyl, alkylphenyl, ether, and azide groups, and combinations thereof.
12. The method of claim 2 wherein the network-forming precursors are charged molecular species.
13. The method of claim 1 wherein the network-forming precursors are polymerizable inorganic species.

14. The method of claim 13, wherein said polymerizable inorganic species are selected from the group consisting of silicon alkoxides, metal alkoxides, metal salts, silicon-metal alkoxides organosiliconalkoxides, organometalalkoxides, and mixtures thereof.

15. The method of claim 13, wherein said polymerizable inorganic species are selected from the group consisting of metal or rare earth salts, alkoxides, sulfides, nitrides and phosphides, and combinations thereof.

16. The method of claim 15, wherein said metal is selected from the group consisting of B, Al, Ca, Cd, Cr, Fe, Ga, Ge, Hf, Mg, Mn, Mo, Nb, P, Sb, Se, Sn, Ta, Ti, V, W, and Zr.

17. The method of claim 1, wherein said combining and treatment steps are conducted under alkaline conditions.

18. The method of claim 17, wherein the pH is in the range of pH 10 to pH 14.

19. The method of claim 1, wherein said mesoscopically structured material formed during the combining step is a hexagonal, cubic, or lamellar mesophase.

20. The method of claim 1, wherein said mesostructured material formed during the treatment step is a lamellar mesophase.

21. The method of claim 1, wherein said treatment involves hydrothermal conditions.

22. The method of claim 21, wherein said hydrothermal conditions include subjecting the material to a temperature of between 100 to 200 degrees Celsius.

23. The method of claim 1, wherein said treatment step is conducted for between one and 120 days.

24. A method of forming a mesophase material having a molecularly ordered silicate framework, comprising:

i) combining a silica precursor, a surfactant having a cationic head group, a base compound, and water under conditions effective to form a mesoscopically structured composite with an amorphous silica framework;

ii) treating the composite under hydrothermal conditions at a temperature of about 100 to 140 degrees Celsius for at least about one day to form a mesophase material having a molecularly ordered silicate framework.

25. The method of claim 24, wherein less than 10% of total silica comprising said mesophase material is amorphous silica.

26. The method of claim 24, wherein the silica precursor is selected from the group consisting of tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), tetrapropoxysilane (TPOS), and sodium silicate.

27. The method of claim 24, wherein said cationic head group is a trialkylammonium moiety.

28. The method of claim 27, wherein said trialkylammonium moiety is selected from the group consisting of trimethylammonium, dimethylethylammonium, diethylmethylammonium, and triethylammonium.

29. The method of claim 24, wherein said base compound is an alkylammonium hydroxide or sodium hydroxide.

30. The method of claim 24, wherein the combining step includes a water miscible organic solvent.

31. The method of claim 30, wherein the organic solvent is an alcohol.

32. The method of claim 24, wherein the combining step includes adjusting the pH to between pH 10 and pH 14.

33. The method of claim 32, wherein the pH is about 11 to 11.5.

34. The method of claim 24, wherein the combining step includes adjusting the ionic strength to promote strong electrostatic interactions between the silicate framework and the surfactant head group.

35. The method of claim 24, wherein said mesophase material is a lamellar mesophase.

36. The method of claim 24, wherein the treatment temperature is about 130 to 140 degrees Celsius.

37. The method of claim 24, wherein the treatment step is conducted for between one and 120 days.

38. The method of claim 28, wherein the trialkylammonium moiety is trimethylammonium, and the treatment step is conducted for about one to two days.

39. The method of claim 28, wherein the trialkylammonium moiety is dimethylethylammonium, and the treatment step is conducted for about three to seven days.

40. The method of claim 28, wherein the trialkylammonium moiety is diethylmethylammonium and the treatment step is conducted for about ten to 20 days.

41. The method of claim 28, wherein the trialkylammonium moiety is triethylammonium, and the treatment step is conducted for about thirteen to 25 days.

42. A mesoscopically structured material containing a molecularly ordered framework made according to claim 1.

43. A mesoscopically structured material containing a molecularly ordered inorganic framework made according to claim 2.

44. The mesoscopically structured material of claim 42, wherein the self-assembly agent is retained in the mesoscopically structured product.

45. The mesoscopically structured material of claim 42, wherein the self-assembly agent is removed from the mesoscopically structured product to form a mesoporous material.

46. A mesoscopically structured material having a molecularly ordered silicate framework made according to claim 24.

47. The mesoscopically structured material of claim 46, wherein the surfactant is removed from the mesophase material to form a mesoporous material.

48. A synthetic mesoscopically structured material, comprising:

i) a self-assembly agent; and

ii) a molecularly ordered inorganic framework other than a naturally occurring mineral structure, said inorganic framework being ordered for a length of greater than one nanometer.

49. The synthetic mesoscopically structured material of claim 48, wherein said molecularly ordered inorganic framework is a crystalline inorganic framework.

50. The synthetic mesoscopically structured material of claim 48, wherein said self-assembly agent is an amphiphilic molecule having one or more hydrophobic chains, one or more of said hydrophilic chains containing charged head groups.

51. The synthetic mesoscopically structured material of claim 48, wherein the inorganic framework is an oxide or mixed oxide.

52. The synthetic mesoscopically structured material of claim 51, wherein said inorganic framework is selected from the group consisting of SiO_2 , TiO_2 , ZrO_2 , SnO_2 , HfO_2 , Al_2O_3 , Ta_2O_5 , V_2O_5 , WO_3 , Nb_2O_5 , $\text{AlSiO}_{3.5}$, $\text{AlSiO}_{5.5}$, SiTiO_4 , ZrTiO_4 , Al_2TiO_5 , rare earth oxides, and mixtures thereof.

53. The synthetic mesoscopically structured material of claim 48, wherein said inorganic framework is a metal oxynitride, metal oxychalcogenide, metal nitride, metal phosphide, metal sulfide, or metal chalcogenide.

54. The synthetic mesoscopically structured material of claim 48, wherein said inorganic framework is a molecularly ordered silicate network.

55. The synthetic mesoscopically structured material of claim 54, wherein less than 10% of total silica comprising said mesoscopically structured material is amorphous silica.

56. The synthetic mesoscopically structured material of claim 50, wherein said inorganic framework is an ordered silicate network, said silicate network having silicon species.

57. The synthetic mesoscopically structured material of claim 56, wherein the silicon species in ordered regions of the ordered silicate framework are located within about one nanometer of the charged head groups of the amphiphilic molecule.

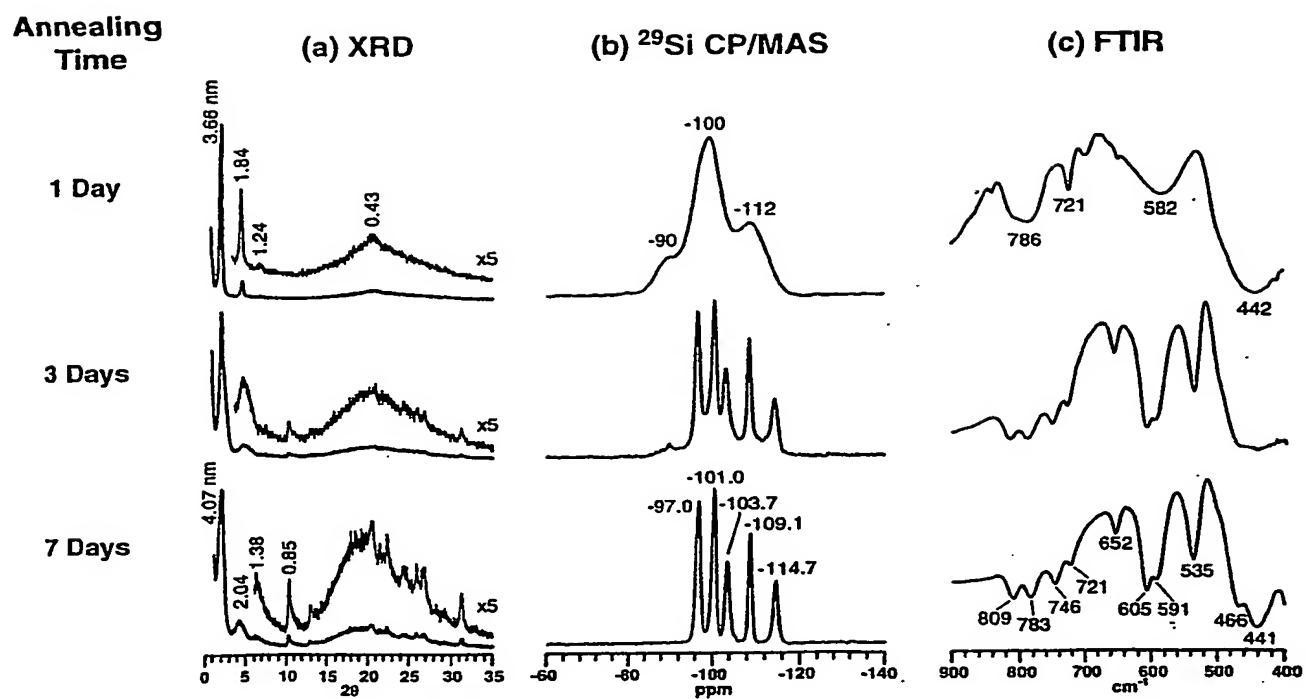


FIG. 1

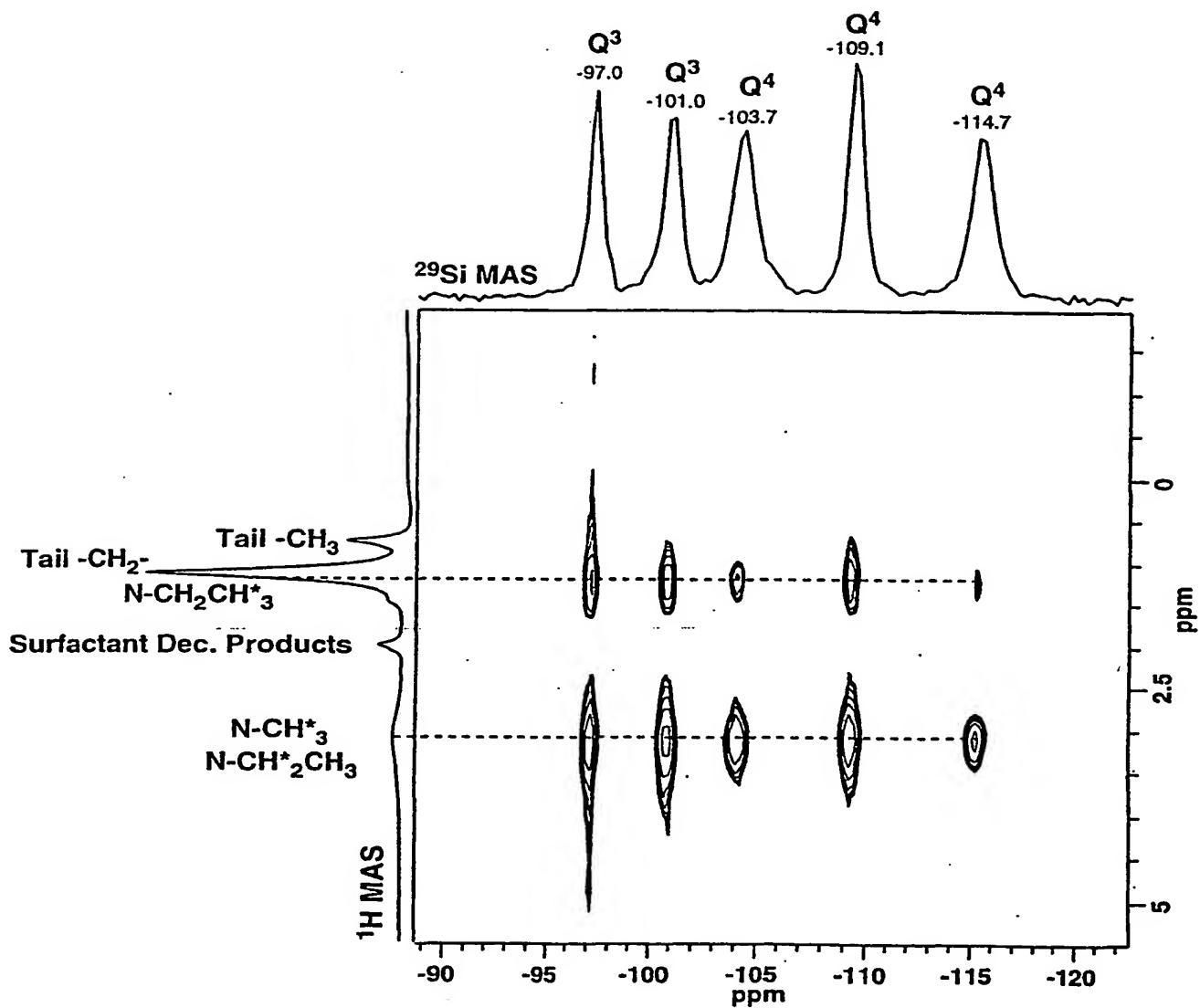


FIG. 2

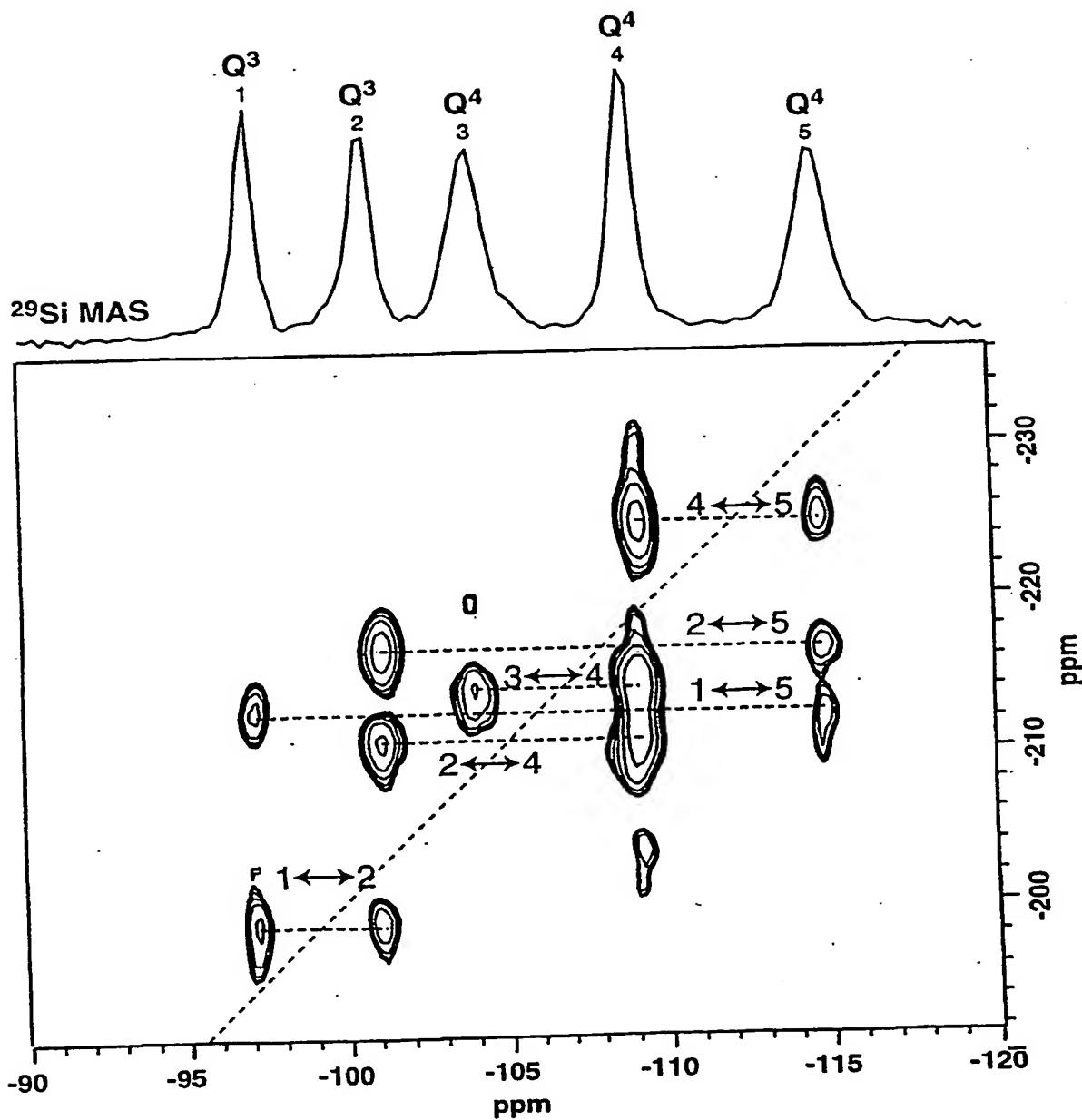


FIG. 3

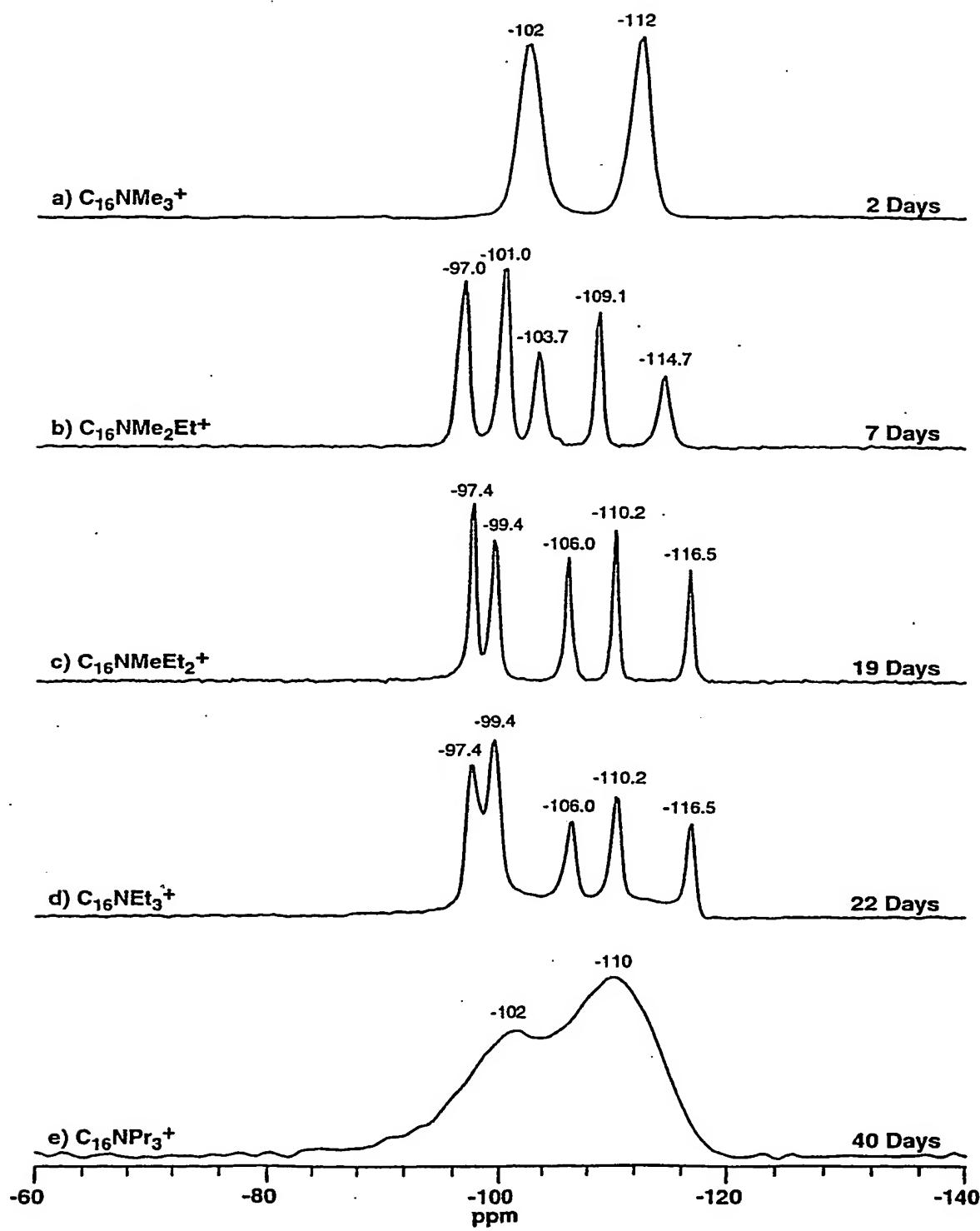


FIG. 4

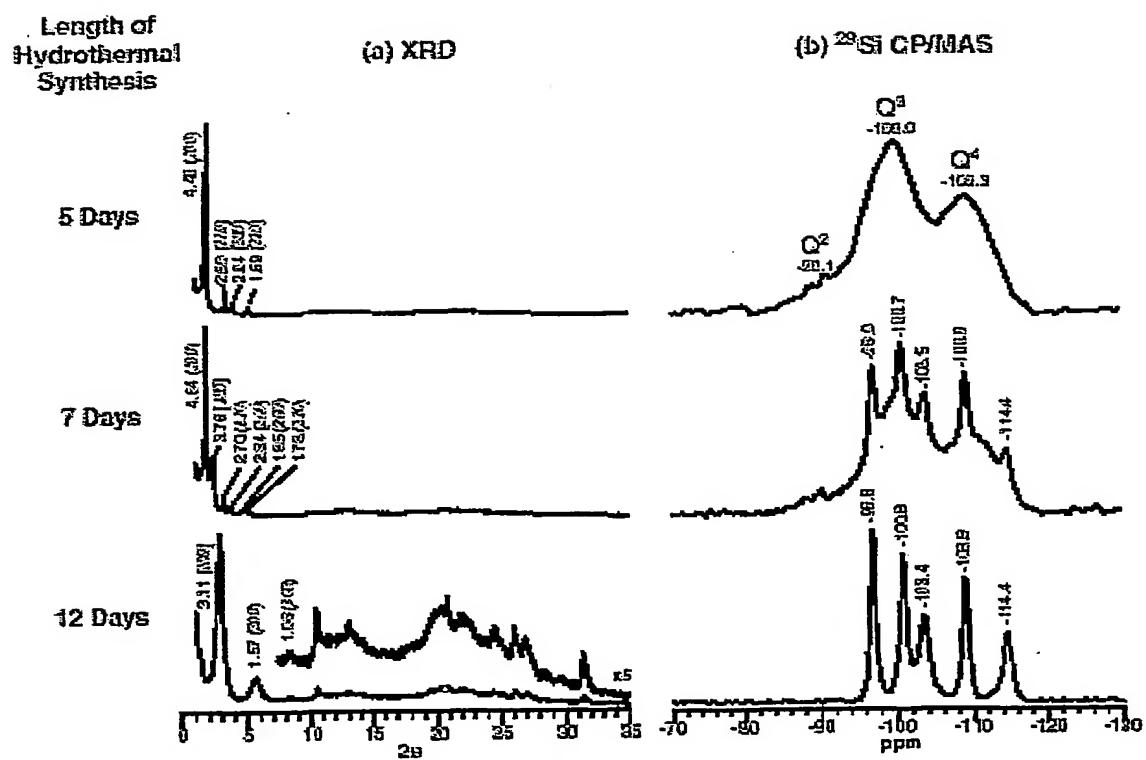


FIGURE 5

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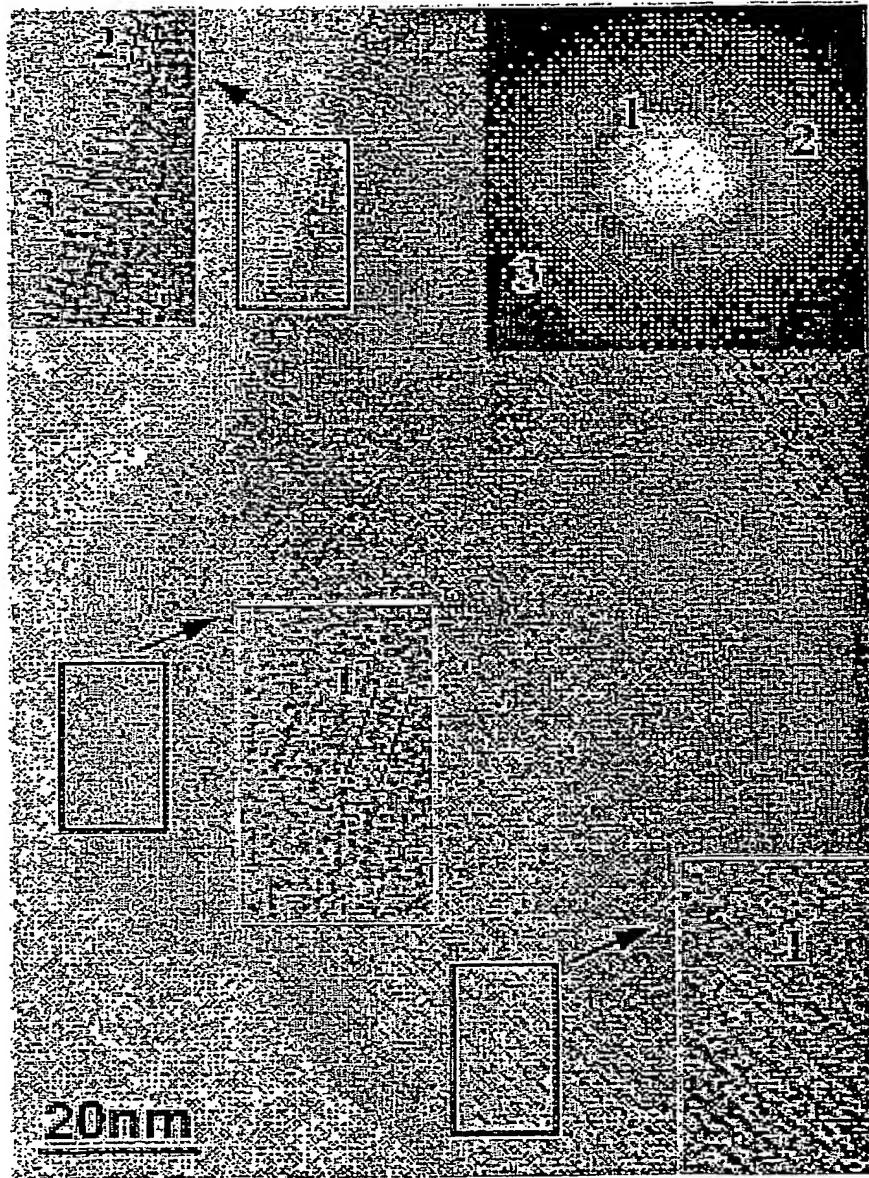
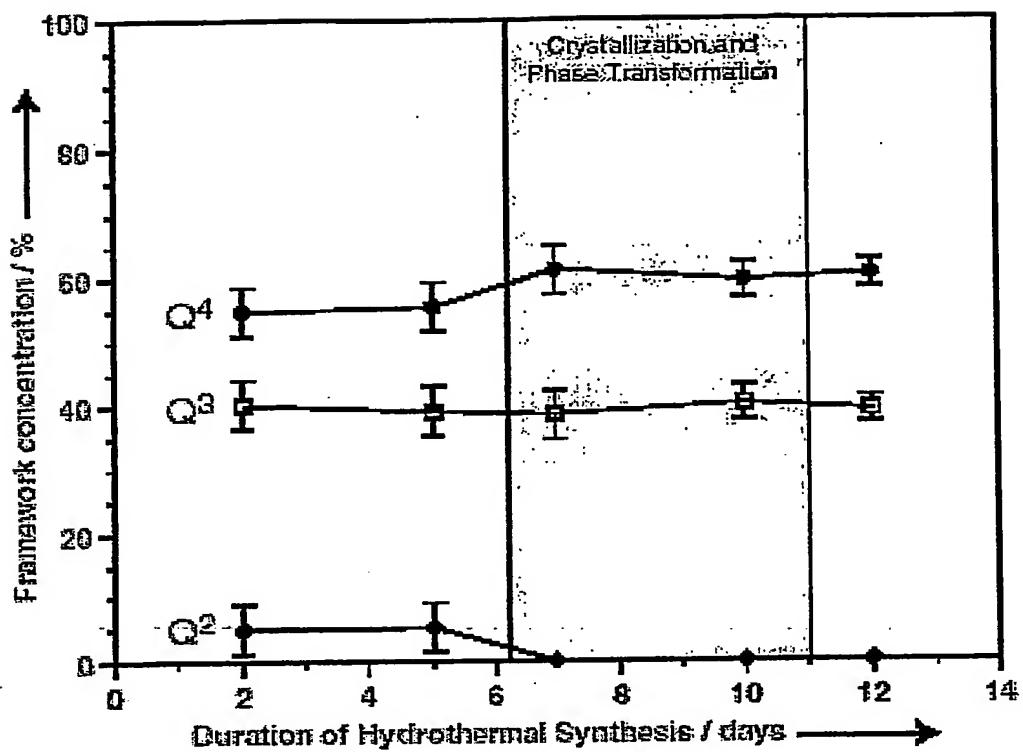


FIGURE 6

**FIGURE 7**

XRD ^{29}Si NMR

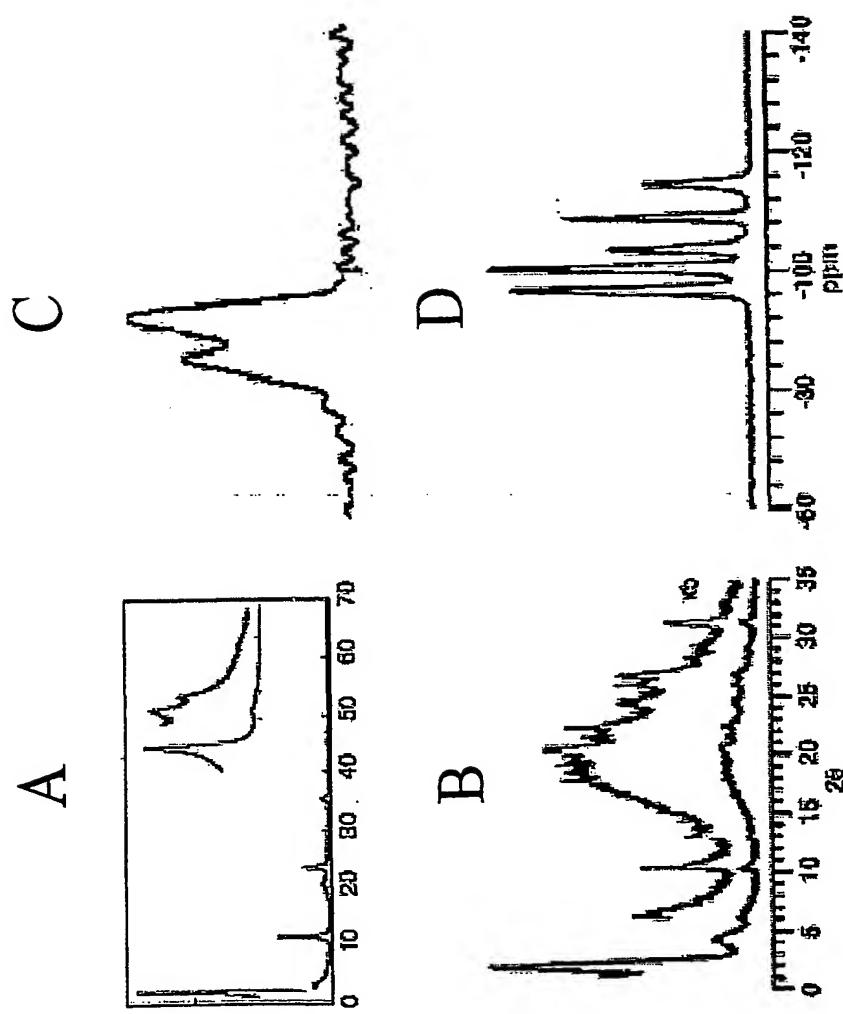


FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/11684

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C25D 1/00; B01D 57/02; C08J 9/26; H01L 21/00
 US CL : 205/687; 204/515; 521/61; 438/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 U.S. : 205/687; 204/515; 521/61; 438/52

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,004,444 A (AKSAY et al) 21 December 1999 (21.12.1999), column 7-14.	1-57
Y	US 6,014,246 A (ASHER et al) 11 January 2000 (11.01.2000), column 4-13.	1-57
Y	US 6,094,273 A (ASHER et al) 25 July 2000 (25.07.2000), column 4-13.	1-57
Y	US 6,099,964 A (BAUMANN et al) 08 August 2000 (08.08.2000), column 2-20.	1-57
A	US 6,187,599 B1 (ASHER et al) 13 February 2001 (13.02.2001), abstract.	1-57
A,P	US 6,331,454 B1 (YAMADA et al) 18 December 2001 (18.12.2001), abstract.	1-57
Y,P	US 6,228,248 B1 (AKSAY et al) 08 May 2001 (08.05.2001), column 2-14.	1-57
A,E	US 6,414,043 B1 (ASHER et al) 02 July 2002 (02.07.2002), column 1-4.	1-57
A	US 5,917,194 A (DUTTA et al) 29 June 1999 (29.06.1999), col. 5.	1-57

<input type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input type="checkbox"/>	See patent family annex.
*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

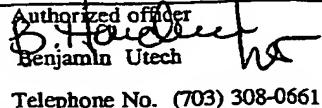
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